Auxiliaries for agrochemical formulations

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3-1 AQUEOUS SOLUTIONS —

Some active ingredients, which are readily soluble and chemically stable in water can be formulated as concentrated solutions. That is the simpliest and the cheapest type of formulation.
However some possible problems needs to be considered:

- the solubility of the active ingredient in the formulation have to be sufficiently high to avoid crystallisation during storage at low temperature.
- The solution diluted at the use rate needs to have a wetting effect on the foliage.

For these reasons to the AQUEOUS SOLUTIONS are often added solubilising agents to improve the solubility at low temperature and sufactants to improve the wetting effect and the penetration of the active ingredient through the cuticular layer.
The wetting agents in our production range are the following:

- **SOPROPHOR 860/P**
- **SOPROPHOR 840**
- **SOPROPHOR BC/10**

As penetration improvers we have:

- **SOPROMINE S/30**
- **SOPROMINE S/35**
- **SOPROMINE O/15**
- **SOPROMINE O/20**

Some more information is given in the chapter: «IMPROVEMENT OF PENETRATION OF CUTICULAR LAYER BY SURFACTANTS» (4.2).

3-2 EMULSIFIABLE CONCENTRATES —

Emulsifiable concentrates, have always been widely used because of their rather simple manufacture process.
Emulsifiable concentrates usually contain:

- active ingredients
- emulsifiers
- stabilizers, stickers, pH buffer etc...
- solvents and cosolvents

The most usual solvents are xylene (usage of this product is now restricted in a number of countries), aromatic solvents such as SOLVESSO, SHELLSOL, etc.
Sometimes to improve the solubility of the active at low temperature it's necessary to add polar solvents such as cyclohexanone, dimethyl-formamide or isophorone etc...

For the application in the field, such a formulation is diluted in water, forming usually an oil-in-water emulsion which permits a uniform distribution of active ingredients on the crop.
The performance of an emulsifier in E.C. is very important to guarantee dispersed phase droplets in the range of O.1. to 5 microns and ensure uniform spreading and wetting which is essential for efficiency. E.C. must always be in compliance with international specifications: F.A.O. (according to CIPAC methods) and W.H.O. They must also be in compliance with those specifically applied in every single country or by every single customer, as long as they respect the under mentioned chemical-physical characteristics:

1) Stability in the long term (2 years approx).
2) Heat stability (54° C).
3) Cold stability (0° C).

When diluted into water, they must have the following characteristics:

1) Good blooming.
2) Good stability to creaming, no oil separation.
3) Behave satisfactorily in water of different hardnesses and temperatures.
4) Perform to the field conditions (different use rates on the field).

3-2-1 EMULSIFIERS RANGE

We list our range of emulsifiers as:

- base emulsifiers.
- blended emulsifiers.

a) *Base emulsifiers*

These are single surfactants, used as a mixture of one or more hydrophilic nonionic surfactants with a lipophilic anionic one. Their balancing is quite critical and the ratios of emulsifiers strictly applied.
Our main base emulsifiers are:

- **NONIONIC**
  - **SOPROPHOR B**
  - **SOPROPHOR OR/36**
  - **SOPROPHOR BSU**
  - **SOPROPHOR S/25**
  - **SOPROPHOR 461/P**
  - **SOPROPHOR 487/P**
  - **SOPROPHOR 497/P**
  - **SOPROPHOR 724/P**

- **ANIONIC**

  - **SOPROPHOR 70**
  - **SOPROPHOR 70/B**
  - **SOPROPHOR 60/BE**
  - **SOPROPHOR 2283**

b) *Blended emulsifiers*

These are blends of anionic and nonionic surfactants, usually with relatively close HLB, used as pairs. Because of their particular compositions, with two or more tensides, their balance is easier and consequently, they offer a wider application field. Blended emulsifiers are also used for some specific formulations which are very difficult to achieve with base emulsifiers.
The main blended emulsifiers we offer are:

Lipophilic activity

- **GERONOL FF/4**
- **GERONOL SC/121**

Hydrophilic activity

- **GERONOL MS**
- **GERONOL FF/6**
- **GERONOL RE/70**
- **GERONOL V/497**
- **GERONOL V/87**

We also developped a similar range of products with a flash point higher than 65° C:

Lipophilic activity

- **GERONOL FF/4-E**
- **GERONOL SC/121-E**

Hydrophilic activity

- **GERONOL MS-E**
- **GERONOL FF/6-E**
- **GERONOL RE/70-E**
- **GERONOL V/497-E**
- **GERONOL V/87-E**

3-2-2 SCREENING OF THE SUITABLE EMULSIFIERS

There are two methods:

3-2-2-1 Practical method based on direct research

According to the following scheme that shows the initial preferential couplings, in relation to their well-known multipurpose activity, prepare:

a) system to emulsify (active ingredients, solvents and stabilizers), containing 5% of a surfactant of table 1.
b) system to emulsify (active ingredients, solvents and stabilizers), containing 5% of a surfactant of table 2.
c) Mix the two solutions according to the known method:

a) system:	10	20	30	40	50	60	70	80	90
b) system:	90	80	70	60	50	40	30	20	10

Find the best balance in order to have a good blooming and consequently good stability to creaming and no oil separation.
If the results are not satisfactory, repeat the test with another nonionic until the suitable pair is found.
Verify eventually, the best ratio of balancing reducing the range of control to 5% (5:95/ 10:90/ 15:85 and so on) instead of 10% as mentioned above.
In some specific cases, it may be necessary to use more than 5% emulsifier to obtain the requested performances.
Increasing the emulsifiers contents provide a better resistance to ageing and reduce variations in performance due to changeable chemical physical characteristics of the components.

— EMULSIFIERS SCREENING SCHEME —

TABLE I	TABLE II
Anionics	*Nonionics*
(Lipophilic activity)	*(Hydrophilic activity)*
BLENDS	
GERONOL FF/4	GERONOL MS
	GERONOL FF/6
	GERONOL RE/70
	GERONOL V/497
BASES	
SOPROPHOR 70	SOPROPHOR OR/36
SOPROPHOR 70/B	SOPROPHOR S/25
SOPROPHOR 2283	SOPROPHOR 497/P
	SOPROPHOR 724/P

The use of above mentioned products usually solves most of the E.C. formulation problems.
Other surfactants (shown in the list of paragraph «Emulsifiers range») could be taken into account, if some particular emulsivity problems occur.
SOPROPHOR 60/BE (alkylaryl sulphonate calcium salt — non flammable) is used mixed with «base emulsifiers» when E.C. with a high flash point is required.
SOPROPHOR 70 (branched) has similar activity of the SOPROPHOR 70/B (linear) and may replace it if the norms of the country allow its utilization.

3-2-2-2 By the HLB determination (HLB system)

It is a long time since the HLB system (hydrophilic-lipophilic balance) was introduced and used, providing reasonable results.
Many specifications and discussions could take place on this principle, also considering the great number of publications issued upon the subject, but its utilisation may be shortly summarised as follows: one should bear in mind that a certain knowledge of the surfactants and of the systems to emulsify is needed in order to use it properly.

a) *Notes on the HLB system*

An arbitrary scale of HLB values is usually abscribed to emulsifiers, ranging from 0 to 20, assuming from 0 to 10 for the lipophil tendency, and from 10 to 20 for the hydrophil tendency.
By using two emulsifiers with a well-known HLB (SOPROPHOR S/25 - SOPROPHOR 70) the HLB of the system to emulsify is determined.
By balancing the surfactants of the «Emulsifiers range» so as to obtain the same HLB, one will find the pair giving the best emulsivity results, which however depend on many factors.

b) *HLB determination of the concentrate to emulsify*

Prepare two solutions having the same E.C. taken into account, the former containing 7% of SOPROPHOR S/25, the latter containing 7% of SOPROPHOR 70, being the most universal matched pair.
Find the best ratio of emulsifier corresponding to the best emulsifiability, in order to determine the optimum HLB.
For this practical research one uses the method cited in «Screening of the suitable emulsifiers» (paragraph 3-2-2-1).
The HLB value is calculated in the following way:

Example:

SOPROPHOR S/25	(HLB 14,5)	- 50%	×	14,5	=	7.25
SOPROPHOR 70	(HLB 8,5)	- 50%	×	8,5	=	4.25

HLB of the mixture 11.50

c) *Determination of the HLB of surface active agents*

There are a number of prescribed methods for rapid theoretical determination of the HLB from knowledge of the molecular structure, e.g.:

$$HLB = \frac{H}{5}$$

«H» being the relative percentage by weight of the hydrophilic moiety in the molecule.

$$HLB = 20\ (1 - \frac{IS}{IA})$$ (valid for ethoxylated fatty acids)

«IS» being the saponification value of the nonionic.
«IA» being the acid value of the fatty acid.
These two formulas can easily be combined.
DAVIES treated the HLB value as a sum of structural factors, each group in the molecule bringing its own contribution to the total HLB value. The following equation allows a good approximation of HLB for most surface active agents.

HLB = 7 + E (Hydrophilic group)—C (lipophilic group).

To have a better chance of obtaining good emulsion, it is advisable to select a surfactant with an HLB value as close as possible to that of the phase to be dispersed.
To give an example, HLB values of several well-known products are shown below.

Disperse phase	*HLB*	*Disperse phase*	*HLB*
Paraffinic oil	10	Solvent naphta	14
Mineral oil	11.5	Benzene	15
Vaseline	12	Diisopropylbenzene	15
Orthodichlorobenzene	13	Toluene	16
Kerosene	14	Pine oil	16
Xylene	14	Essential oils	15-17

3-2-3 CONTROL METHODS

There are different control methods existing, which some large manufacturers and countries usually refer to, in compliance with the particular environmental and legislative requirements.
The formulations listed in this catalogue have been specifically designed in order to achieve the best performances by using the official CIPAC control methods which, on average, better summarise the different norms.
The qualitative specifications which the E.C. must show, can be generally summarised and simplified as follows:

1) Limpid product, without suspended matter or sediment.
2) Active ingredient content.
3) Emulsion stability and re-emulsion: (CIPAC 1-MT 36).
4) pH: (CIPAC 1-MT 75).
5) Storage: low temperature stability: (CIPAC 1-MT 39).
high » » (CIPAC 1-MT 46.1.3).

The formulations subjected to accelerated storage test by heating might show slight chemical-physical variations to items 1, 2, 3, 4 and, however, comply with the FAO specifications or close values when not edited.
Better performances could be achieved with components of changeable chemical-physical characteristics, water with different hardnesses and temperatures, by balancing the ratios of the emulsifiers.

EMULSIFIABLE CONCENTRATES - 3.2

Active Ingredients		Emulsifiers						Stabilizers and solvents		
		FF/4	FF/6	MS	V/497	V/87	---	---	Xylene	Shellsol ab
Acetochlor	50	2,5				4,0		MCB. up to 100		
Alachlor	48	2,2				2,8		MCB. up to 100		
Azinphos Ethyl	20	2,0		3,0					up to 100	
Azinphos Methyl	20	1,0		8,0				MCB. up to 100		
Butachlor	60	4,0	2,0						up to 100	
Carbophenothion	46	3,6			2,4				up to 100	
Chlorfenson	30	2,5	7,5						up to 100	
Chlordane	75	5,8				4,2		EPO. 1	up to 100	
Chlorobenzilate	50	1,6		4,5					up to 100	
Chlorpyrifos Ethyl	48	3,2					RE/70 1,8		up to 100	
Cypermethrin	10	2,7		3,3					up to 100	
Cypermethrin	25	3,0		3,0					up to 100	
Cypermethrin	10	3,3		2,7						up to 100
Cypermethrin	25	3,6		2,4						up to 100
Diazinon	60	3,0		2,4				EPO. 2	up to 100	
Dichlorvos	50				3,7		OR/36 : 2,3	EPO. 2	up to 100	
Dicofol	18,5	0,7		6,3					up to 100	
Dicofol	48	2,6				9,4		Cyclohexanone 26	up to 100	
Dicofol/Tetradifon	16/6	0,6		5,4					up to 100	
Dimethoate	40						SC/167 : 5,0	Cyclohexanone 40	up to 100	
Dinocap	48	1,0		4,0					up to 100	
2-4 D Isooctyl Ester	50	1,7		3,3						up to 100